

LETTER TO THE EDITOR

The decay of photoexcited quantum systems: a description within the statistical scattering model

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Abstract. The decay of photoexcited quantum systems (examples are photodissociation of molecules and autoionization of atoms) can be viewed as a half-collision process (an incoming photon excites the system which subsequently decays by dissociation or autoionization). For this reason, the standard statistical approach to quantum scattering, originally developed to describe nuclear compound reactions, is not directly applicable. Using an alternative approach, correlations and fluctuations of observables characterizing this process were first derived in [Fyodorov YV and Alhassid Y 1998 *Phys. Rev. A* **58** R3375]. Here we show how the results cited above, and more recent results incorporating direct decay processes, can be obtained from the standard statistical scattering approach by introducing one additional channel.

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Molecular photodissociation [1, 2, 3, 4, 5, 6] and atomic autoionization [7] are examples of quantum-mechanical decay processes: excited quantum systems decay into one or several scattering continua (decay channels). The situation is illustrated schematically in figure 1. An atom or a molecule is excited from its ground state or a low lying state $|g\rangle$ by a photon. Photoabsorption either results in direct excitation of the decay channels $|E_a\rangle$ (where $a = 1, \dots, M$) or in excitation of quasi-bound states $|n\rangle$ (where $n = 1, \dots, N$). Decay into a channel $|E_a\rangle$ then proceeds via residual interactions between the quasi-bound states and the continua.

Correlations and fluctuations of the quasi-bound states determine the statistical properties of the indirect decay cross section. If the corresponding classical dynamics is sufficiently chaotic, these properties can be modeled by random matrix theory [8, 9, 10]. In reference [11] this approach was adopted to characterize the distribution and two-point correlations of the indirect photodissociation cross-section, in the absence of direct decay channels. The results of [11] were obtained by calculating the statistical properties of a resolvent of an effective non-Hermitian Hamiltonian. Equivalently they may be obtained from eigenvector correlations [12, 13, 14] of the non-Hermitian effective Hamiltonian. In the limit of weak continuum coupling, cross-section correlations can be calculated using perturbation theory [15]. The results of reference [15] have been generalized in [16] where interference effects between direct and indirect decay paths in the photoabsorption cross section were studied.

How are the results obtained in [11, 15, 16] related to those derived for nuclear and mesoscopic scattering processes within the so-called statistical scattering model (also termed the Heidelberg model [17, 18, 19, 10])? Since photodecay is a half-collision process [20, 21], the statistical scattering model as such is not directly applicable. In order to establish a connection to the statistical scattering model, it has been suggested [22] to introduce an additional channel representing photoexcitation. In this paper we show how to describe the decay of photoexcited quantum systems using this idea. Our results can be summarized as follows: We demonstrate that partial and total decay cross sections can be obtained from an extended (almost) unitary scattering matrix by introducing an additional channel for photoexcitation and a linear transformation reminiscent of the “Engelbrecht-Weidenmüller” transformation [23]. We use that relation to obtain a non-perturbative result for the two-point correlation function of the total cross section in a random-matrix model, which allows for arbitrary coupling strengths between quasi-bound states, decay channels and the photoexcited initial state.

Let $|\alpha\rangle = \hat{\mu}|g\rangle$ be the ground state dressed with the dipole operator $\hat{\mu}$. The partial photodissociation (photoionization) cross section into channel a is proportional to [21, 24]

$$\sigma_a(E) \propto \left| \langle \alpha | \Psi^{(a)}(E) \rangle \right|^2, \quad (1)$$

where the scattering wave function $|\Psi^{(a)}\rangle$ is outgoing in channel a only. The total photodissociation cross section is given by

$$\sigma(E) = \sum_{a=1}^M \sigma_a(E) \quad (2)$$

(M is the number of open channels). We follow the approach adopted in [11, 16] where resonant and direct processes were treated separately by means of the Feshbach approach [25]: the Hilbert space of excited states is divided into a subspace of

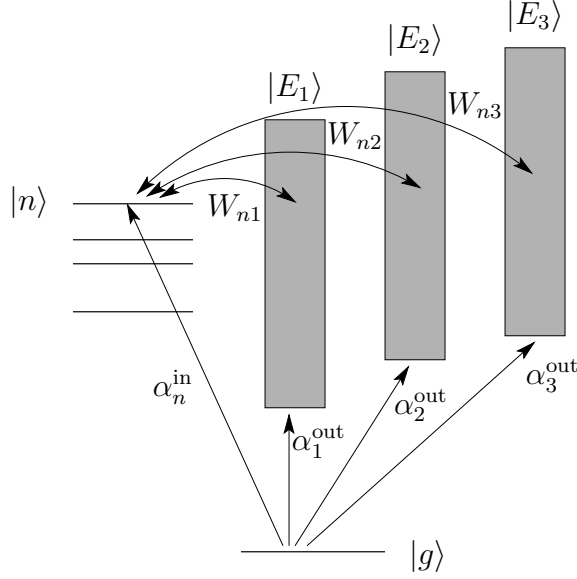


Figure 1. Direct photoionization from an initial state $|g\rangle$ into the subspace of unbound states (M continuum channels $|E_a\rangle$, here: $M = 3$) with transition amplitudes α_a^{out} , and indirect photoionization via N bound states $|n\rangle$ with transition amplitudes α_n^{in} . The states $|n\rangle$ turn into resonances due to couplings to the continua with matrix elements W_{na} .

bound states, and its complement containing all unbound states. The vector $|\alpha\rangle$ is decomposed accordingly $|\alpha\rangle = |\alpha^{\text{in}}\rangle \oplus |\alpha^{\text{out}}\rangle$. Choosing the bound space appropriately, the scattering problem projected onto the complement loses all resonant features. The Hamilton operator in the bound space is represented by an $N \times N$ random matrix \mathbf{H}_0 , with eigenstates $|n\rangle$, $n = 1, \dots, N$. The N dipole transition matrix elements to $|n\rangle$ are denoted by α_n^{in} , and $\boldsymbol{\alpha}^{\text{in}} = (\alpha_1^{\text{in}}, \dots, \alpha_N^{\text{in}})^T$. Correspondingly, the M (energy-independent) dipole transition matrix elements from $|g\rangle$ to the decay channels are α_a^{out} , and $\boldsymbol{\alpha}^{\text{out}} = (\alpha_1^{\text{out}}, \dots, \alpha_M^{\text{out}})^T$. The matrix elements of the residual interaction \hat{W} are denoted by $W_{na} = \langle n | \hat{W} | E_a \rangle$, and $\mathbf{W}_a = (W_{1a}, \dots, W_{Na})^T$ are the column vectors of \mathbf{W} . For the total cross section, the following result has been obtained in [16]:

$$\sigma(E) = \|\boldsymbol{\alpha}^{\text{out}}\|^2 - \pi^{-1} \text{Im} \left[(\boldsymbol{\alpha}^{\text{in}} + i\pi \mathbf{W} \boldsymbol{\alpha}^{\text{out}})^\dagger \frac{1}{E - \mathbf{H}_{\text{eff}}} (\boldsymbol{\alpha}^{\text{in}} - i\pi \mathbf{W} \boldsymbol{\alpha}^{\text{out}}) \right]. \quad (3)$$

Here $\mathbf{H}_{\text{eff}} = \mathbf{H}_0 - i\pi \mathbf{W} \mathbf{W}^\dagger$ is an effective non-Hermitian Hamiltonian. The partial cross section is given by

$$\sigma_a(E) = \left| \alpha_a^{\text{out}} + \mathbf{W}_a^\dagger \frac{1}{E - \mathbf{H}_{\text{eff}}} (\boldsymbol{\alpha}^{\text{in}} - i\pi \mathbf{W} \boldsymbol{\alpha}^{\text{out}}) \right|^2. \quad (4)$$

It can be shown by purely algebraic manipulations that, indeed, $\sum_{a=1}^M \sigma_a(E) = \sigma(E)$.

We now prove that the cross sections given in (3) and (4) can be expressed in terms of the extended $(1+M) \times (1+M)$ unitary scattering matrix

$$\mathbf{S}(E, \delta) = \mathbf{1}_{1+M} - 2i\pi \mathbf{V}^\dagger \frac{1}{E - \mathbf{F}_{\text{eff}}} \mathbf{V} \quad \text{with} \quad \mathbf{V} = (\boldsymbol{\alpha}^{\text{in}} \delta / 2\pi, \mathbf{W}), \quad (5)$$

and $\mathbf{F}_{\text{eff}} = \mathbf{H}_0 - i\pi \mathbf{V} \mathbf{V}^\dagger$. This maps our problem onto the statistical scattering model. It is convenient to enumerate the channels from 0 to M , so that the new channel, referring to photoexcitation, gets the index 0. The corresponding column vector of \mathbf{V} is scaled with a real positive parameter δ (which will be taken to zero at the end of the calculation). Now, consider transform $\mathbf{S}'(E, \delta) = \mathbf{u}(\delta) \mathbf{S}(E, \delta) \mathbf{v}^T(\delta)$, where the matrices $\mathbf{u}(\delta)$ and $\mathbf{v}(\delta)$ are given by

$$\mathbf{u}(\delta) = \left(\begin{array}{c|c} \begin{matrix} i \\ 0 \\ \vdots \\ 0 \end{matrix} & \begin{matrix} (\boldsymbol{\alpha}^{\text{out}})^\dagger \delta/2 \\ \mathbf{1}_M \end{matrix} \end{array} \right), \quad \mathbf{v}(\delta) = \left(\begin{array}{c|c} \begin{matrix} i \\ 0 \\ \vdots \\ 0 \end{matrix} & \begin{matrix} (\boldsymbol{\alpha}^{\text{out}})^T \delta/2 \\ \mathbf{1}_M \end{matrix} \end{array} \right). \quad (6)$$

The transformation (6) is reminiscent of an ‘‘Engelbrecht-Weidenmüller’’ transformation [23], although for $\delta > 0$, $\mathbf{u}(\delta)$ and $\mathbf{v}(\delta)$ are not unitary. We now show that the cross sections (3) and (4) can be expressed in terms of the elements of $\mathbf{S}'(E, \delta)$ as follows

$$\sigma_a(E) = \lim_{\delta \rightarrow 0} \delta^{-2} \left| \frac{\delta}{2} \alpha_a^{\text{out}} + S'_{a0}(E, \delta) \right|^2 \quad (7)$$

$$\sigma(E) = 2 \lim_{\delta \rightarrow 0} \delta^{-2} \left[\frac{\delta^2}{4} \|\boldsymbol{\alpha}^{\text{out}}\|^2 + 1 + \text{Re } S'_{00}(E, \delta) \right]. \quad (8)$$

In order to derive these relations, we compute the corresponding matrix elements of $\mathbf{S}'(E, \delta)$. Let $1 \leq a \leq M$:

$$\begin{aligned} S'_{a0}(E, \delta) &= \sum_{b,c=0}^M u_{ab}(\delta) S_{bc}(E, \delta) v_{0c}(\delta) = i S_{a0}(E, \delta) + \sum_{c=1}^M S_{ac}(E, \delta) \frac{\delta}{2} \alpha_c^{\text{out}} \\ &= \frac{\delta}{2} \alpha_a^{\text{out}} + \delta \mathbf{W}_a^\dagger \frac{1}{E - \mathbf{F}_{\text{eff}}} (\boldsymbol{\alpha}^{\text{in}} - i\pi \mathbf{W} \boldsymbol{\alpha}^{\text{out}}) \end{aligned} \quad (9)$$

$$\begin{aligned} S'_{00}(E, \delta) &= -S_{00}(E, \delta) + i \frac{\delta}{2} \sum_{b=1}^M [(\alpha_b^{\text{out}})^* S_{b0}(E, \delta) + S_{0b}(E, \delta) \alpha_b^{\text{out}}] \\ &\quad + \frac{\delta^2}{4} \sum_{b,c=1}^M (\alpha_b^{\text{out}})^* S_{bc}(E, \delta) \alpha_c^{\text{out}} \\ &= -1 + i \frac{\delta^2}{2\pi} (\boldsymbol{\alpha}^{\text{in}})^\dagger \frac{1}{E - \mathbf{F}_{\text{eff}}} \boldsymbol{\alpha}^{\text{in}} \\ &\quad + \frac{\delta^2}{2} \left[(\boldsymbol{\alpha}^{\text{out}})^\dagger \mathbf{W}^\dagger \frac{1}{E - \mathbf{F}_{\text{eff}}} \boldsymbol{\alpha}^{\text{in}} + (\boldsymbol{\alpha}^{\text{in}})^\dagger \frac{1}{E - \mathbf{F}_{\text{eff}}} \mathbf{W} \boldsymbol{\alpha}^{\text{out}} \right] \\ &= -1 + \frac{\delta^2}{4} \|\boldsymbol{\alpha}^{\text{out}}\|^2 + \frac{i\delta^2}{2\pi} (\boldsymbol{\alpha}^{\text{in}} + i\pi \mathbf{W} \boldsymbol{\alpha}^{\text{out}})^\dagger \frac{1}{E - \mathbf{F}_{\text{eff}}} (\boldsymbol{\alpha}^{\text{in}} - i\pi \mathbf{W} \boldsymbol{\alpha}^{\text{out}}). \end{aligned} \quad (10)$$

Since $\mathbf{F}_{\text{eff}} \rightarrow \mathbf{H}_{\text{eff}}$ in the limit $\delta \rightarrow 0$, we obtain expressions (3) and (4) for the cross sections. This is easily verified by inserting (9) and (10) into the left hand side of (7) and (8), respectively.

Equations (7) and (8) enable us to compute the average total cross section, as well as its correlation function, defined as

$$C(E, w) = \langle \sigma(E - w \Delta/2) \sigma(E + w \Delta/2) \rangle - \langle \sigma(E) \rangle^2. \quad (11)$$

Here Δ is the average local distance between neighboring resonances, and $\langle \dots \rangle$ denotes an energy average, often replaced by an ensemble average in theory. For simplicity,

we assume that the column vectors of \mathbf{V} in equation (5) are pairwise orthogonal (see below). In this case, the average extended scattering matrix $\langle S(E, \delta) \rangle$ is real and diagonal, with diagonal elements given by [26]

$$\langle S_{aa}(E, \delta) \rangle = \frac{1 - \lambda_a}{1 + \lambda_a}, \quad \lambda_a = \pi^2 \varrho_0 \|W^{(a)}\|^2, \quad \text{and} \quad \lambda_0 = \frac{\delta^2}{4} \varrho_0 \|\boldsymbol{\alpha}^{\text{in}}\|^2, \quad (12)$$

where $N\varrho_0 = 1/\Delta$ is the level density. Starting from equation (8) and assuming that \mathbf{H}_0 corresponds to a classically chaotic system, we obtain the expression for the average total cross section derived in [16]:

$$\begin{aligned} \langle \sigma(E) \rangle &= \frac{\|\boldsymbol{\alpha}^{\text{out}}\|^2}{2} + \lim_{\delta \rightarrow 0} \frac{2}{\delta^2} \left[1 + \sum_{a,b=0}^M \text{Re} \left[u_{0a} v_{0b} \langle S_{ab}(E, \delta) \rangle \right] \right] \\ &= \|\boldsymbol{\alpha}^{\text{out}}\|^2 + \varrho_0 \|\boldsymbol{\alpha}^{\text{in}}\|^2 - \sum_{a=1}^M |\alpha_a^{\text{out}}|^2 \frac{\lambda_a}{1 + \lambda_a}. \end{aligned} \quad (13)$$

In a similar way, we may write for the autocorrelation function of $\sigma(E)$

$$\begin{aligned} C(E, w) &= \lim_{\delta \rightarrow 0} \frac{2}{\delta^4} \sum_{a,b=0}^M \sum_{c,d=0}^M u_{0a}(\delta) u_{0c}(\delta) v_{0b}(\delta) v_{0d}(\delta) \\ &\quad \times \text{Re} \left[\langle S_{ab}(E - w\Delta/2) S_{cd}^*(E + w\Delta/2) \rangle - \langle S_{ab}(E) \rangle \langle S_{cd}^*(E) \rangle \right]. \end{aligned} \quad (14)$$

It has been used that the correlation function of two S -matrix elements is different from zero only if one S -matrix element is complex conjugated while the other is not (see reference [26] for details). Equation (14) expresses the autocorrelation function of the total absorption cross section in terms of correlation functions of elements of the extended scattering matrix, defined in (5). Usually, the energy dependence of the autocorrelation function is mainly due to the energy dependence of the coupling parameters $\boldsymbol{\alpha}^{\text{out}}$, $\|\boldsymbol{\alpha}^{\text{in}}\|^2$ and $\lambda_1, \dots, \lambda_M$. This dependence should be weak in order to allow energy averaging over a sufficiently large window. In cases where the corresponding S -matrix correlation functions are available, equation (14) enables us to obtain the autocorrelation function of the total cross section in closed form.

As an illustration, let us assume time-reversal invariance for the collisional system and predominantly chaotic dynamics in the large ($N \rightarrow \infty$) bound space. Then, the required S -matrix correlation functions are given by the Verbaarschot-Weidenmüller-Zirnbauer (VWZ) integral [18]. Using a Fourier representation developed in [26] we obtain:

$$\begin{aligned} C(E, w) &= 4 \int dt e^{-2\pi i wt} \int_{\max(0, t-1)}^t dr \int_0^r du \frac{(t-r)(r+1-t)}{(2u+1)(t^2-r^2+x)^2} \prod_{e=1}^M \frac{1 - T_e(t-r)}{(1 + 2T_e r + T_e^2 x)^{1/2}} \\ &\quad \times \left\{ \left(\Delta_0 - \frac{1}{4} \sum_{a=1}^M \tau_a \sqrt{1 - T_a} \Delta_a \right)^2 + \Pi_{00} + \sum_{a=1}^M \frac{\tau_a}{2} \Pi_{0a} + \sum_{a,b=1}^M \frac{\tau_a \tau_b}{16} \Pi_{ab} \right\} \end{aligned} \quad (15)$$

where $x = u^2(2r+1)/(2u+1)$, and where $\tau_a = T_a |\alpha_a^{\text{out}}|^2 / (\varrho_0 \|\boldsymbol{\alpha}^{\text{in}}\|^2)$. As usual, it is more convenient to work with the transmission coefficients $T_a = 4\lambda_a/(1 + \lambda_a)^2$ to describe the coupling between the subspace of quasi-bound states and the decay channels. The functions Δ_a and Π_{ab} are defined as follows:

$$\Delta_a = \frac{r + T_a x}{1 + T_a(2r + T_a x)} + \frac{t - r}{1 - T_a(t - r)}$$

$$\Pi_{ab} = \frac{T_a T_b x^2 + [T_a T_b r + (T_a + T_b)(r + 1) - 1]x + r(2r + 1)}{(1 + 2T_a r + T_a^2 x)(1 + 2T_b r + T_b^2 x)} + \frac{(t - r)(r + 1 - t)}{[1 - T_a(t - r)][1 - T_b(t - r)]} . \quad (16)$$

In the special case of $M = 1$ open channel, a result corresponding to (15,16) was derived, by a different approach, in [27]. In the absence of direct processes (i.e., when all direct dipole transition amplitudes α_j^{out} are zero) equation (15) reduces to the result derived in [11]. Note that in (16), the limit $\delta \rightarrow 0$ has been taken. This implies that the transmission coefficient corresponding to the “photo channel” has to be set to zero.

In figure 2, the correlation function $C(E, \omega)$ is shown: as obtained from equation (15), valid in the limit of $N \rightarrow \infty$, and as obtained from the numerical diagonalisation of finite matrices of size $N = 128$. In the presence of direct decay channels, finite-size effects are seen to be somewhat larger, as compared with purely indirect decay.

We conclude with two remarks. First, the VWZ-integral can also be used to calculate the average of the partial photoabsorption cross sections. However, for the correlation functions of the partial cross sections no exact analytical formulae are known. In this case one must use approximate results, such as the “rescaled” Breit-Wigner approximation [15, 26]. Second, in theoretical studies of the statistical scattering model, it is often assumed that the channel vectors (the column vectors of \mathbf{V}) are orthogonal to each other: one can always obtain the original scattering matrix by an appropriate unitary transformation from a simpler scattering matrix with orthogonal channel vectors.

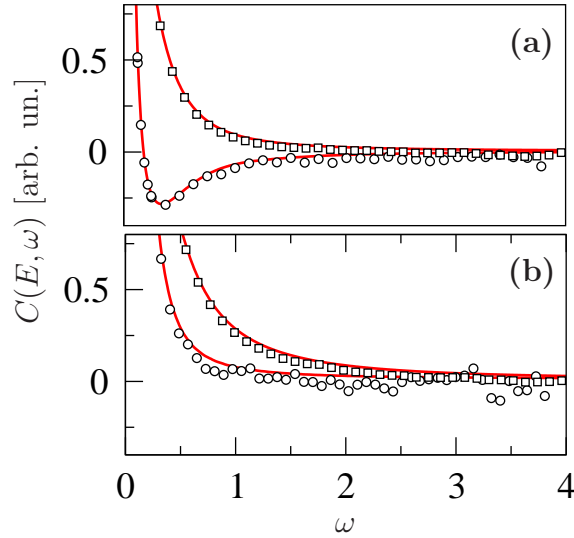


Figure 2. Correlation function (11) of the total cross section, time-reversal invariant case, results according to equation (15) (lines) and from the numerical diagonalisation of random matrices with $N = 128$ (symbols). **(a)**: without direct coupling ($\alpha^{\text{out}} = 0$), $M = 2$, $\gamma = 0.02$ (\circ), and $\gamma = 0.5$ (\square). **(b)**: with direct coupling, $M = 2$, $\gamma = 0.02$, $\alpha_j^{\text{out}} = 2.5$ (\circ), and $\gamma = 0.5$, $\alpha_j^{\text{out}} = 0.5$ (\square).

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